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NITROGEN TRIFLUORIDE: ITS CHEMISTRY, TOXICITY, AND SAFE HANDLING

BY FRANK J. PISACANE
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RESEARCH AND TECHNOLOGY DEPARTMENT

12 NOVEMBER 1976

NAVAL SURFACE WEAPONS CENTER
Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

14

1. REPORT NUMBER
NSWC/WOL/MP-76-24

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

9

6

4. TITLE (and Subtitle)
NITROGEN TRIFLUORIDE: ITS CHEMISTRY, TOXICITY, AND SAFE HANDLING.

5. TYPE OF REPORT & PERIOD COVERED
Summary Report.
Mar 1974 - Aug. 1975,

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
Frank Pisacane, Ottmar H. Dengel, Edward Baroody, Robert Robb, Barry Pallay, William Gilligan, George Wilmot, Anthony Rowek

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Naval Surface Weapons Center
White Oak Laboratory
White Oak, Silver Spring, Maryland 20910

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
ONN; ~~0~~;
/092-1F-SL40AA76; DN484056;

11. CONTROLLING OFFICE NAME AND ADDRESS

11

12. REPORT DATE
12 November 1976

13. NUMBER OF PAGES
25

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

12 31p.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

10 Frank J./Pisacane, Edward/Baroody, Robert/Robb, Ottmar H./Dengel William/Gilligan

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nitrogen trifluoride; Flammability limits; Compatibility; Corrosion; Toxicity; Detection: Monitoring: Disposal: Fire-fighting

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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the Naval Surface Weapons Center, an experimental program was conducted to: (1) determine safety and compatibility characteristics of NF_3 under various conditions with gases, liquids, and solids with which it might come into contact; (2) survey the available toxicity data; (3) develop adequate detection techniques; and (4) recommend safe handling, fire-fighting, and emergency disposal methods.

NSWC/WOL/MP 76-24

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Distribution unlimited. Date statement applied 12 November 1976. Other requests for this publication must be referred to NAVSURFWPNCEN/WOL, Code WR20.

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ABSTRACT

Nitrogen trifluoride (NF_3) is the most promising near-term replacement for fluorine in a DF chemical laser. Safety and compatibility characteristics of NF_3 have been scattered through the literature since the gas was first prepared by Ruff in 1928. Most of the data have been obtained to outline the general chemical behavior of NF_3 and leave many critical safety, compatibility and environmental questions unanswered. Moreover, some of the data found in the literature are erroneous. As part of the Advance Reactants Program at the Naval Surface Weapons Center, an experimental program was conducted to: (1) determine safety and compatibility characteristics of NF_3 under various conditions with gases, liquids, and solids with which it might come into contact; (2) survey the available toxicity data; (3) develop adequate detection techniques; and (4) recommend safe handling, fire-fighting, and emergency disposal methods.

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INTRODUCTION

From the standpoint of safety and handling, nitrogen trifluoride (NF_3) is the most promising near-term replacement for fluorine as a pre-combustor oxidizer in a DF chemical laser. Since NF_3 was first prepared by Ruff in 1928[1], safety and compatibility data have been scattered through the literature, but most of these data were obtained to outline the general chemical characteristics of the gas. A survey of available information on the properties and behavior of NF_3 under various conditions has revealed that the reported physical and chemical data are at best incomplete. Inconsistencies exist, and some data are even incorrect. Conclusions based on these data may create hazardous situations. In addition, many critical safety, compatibility, and environmental questions remain unanswered.

As a part of the Advanced Reactants Program at the Naval Surface Weapons Center, an experimental program was undertaken to better characterize NF_3 and to identify potential hazards involved in its use. Specific areas of concern were: the determination of safety and compatibility characteristics of NF_3 with gases and condensed matter with which it might come into contact; the compilation and evaluation of available toxicity data; the detection and monitoring of NF_3 leaks into the atmosphere; and the identification of safe handling, fire-fighting, and emergency disposal techniques.

DISCUSSION

I. Safety and Compatibility of NF_3

Tests were conducted to determine some of the safety and compatibility characteristics of NF_3 with a variety of gases and condensed matter[2]. At room temperature NF_3 appears to be relatively inert towards most materials; however, slow reactions may occur over long exposures. This relative inertness enables NF_3 to mix with gaseous fuels, forming highly flammable or explosive compositions that are sensitive to spark, heat, or impact. As the temperature is increased, NF_3 becomes a stronger fluorinating agent. Rapid reactions begin to occur at about 250 - 350°C. If the temperature is sufficiently high, NF_3 can be expected to ignite most materials with which it comes into contact. The chemistry of its reactions is different than that of either oxygen or fluorine and caution must be taken when drawing analogies.

I.A. Reactions of NF_3 with Gases

Ruff et al[3,4] have reported that mixtures of NF_3 with H_2, CH_4, C_2H_2, CO, H_2S or NH_3 do not react at room temperature but explode violently when exposed to an electric discharge. Mixtures of NF_3 with ClF or SO_2 appeared to be inert. Water vapor and NF_3 were reported to ignite when sparked and burned with a brown flame according to Equation 1; howevever, the reaction

shown by Equation 2 is thermodynamically more favored. Tompkins et al[5] have reported the range of flammability of NF_3/H_2 mixtures to be from 9.4 to 95 mole percent H_2. The heat released for complete fuel consumption is given in Equation 3, and the effect of adding nitrogen diluent on the flammability limits is shown in Figure 1. (In Figures 1 through 4, the shaded areas represent mixtures that will propagate combustion by either flame or explosion. The lines labeled "S" indicated stoichiometric mixtures of oxidizer and fuel.) For comparison, the range of flammability of hydrogen/oxygen mixtures and hydrogen/air mixtures are 4.0 to 96 and 4.0 to 75 mole percent hydrogen, respectively[6]. A diagram very similar to Figure 1 can be constructed for $O_2/H_2/N_2$ mixtures, and it is tempting to estimate that the flammability hazards of NF_3/fuel mixtures are closely approximated by those of O_2/fuel mixtures. Such a comparison is not valid.

Eq. 1: $H_2O + 2/3\ NF_3 \longrightarrow 2HF + 1/3\ NO + 1/3\ NO_2$ -33.9 kcal

Eq. 2: $H_2O + 2/3\ NF_3 \longrightarrow 2HF + 1/2\ O_2 + 1/3\ N_2$ -41.5 kcal

Eq. 3: $H_2 + 2/3\ NF_3 \longrightarrow 2HF + 1/3\ N_2$ -109.8 kcal

Eq. 4: $C_4H_{10} + 26/3\ NF_3 \longrightarrow 10HF + 4\ CF_4 + 13/3\ N_2$ -1252.8 kcal

Eq. 5: $C_4H_{10} + 13/2\ O_2 \longrightarrow 5H_2O + 4\ CO_2$ -688.0 kcal

Eq. 6: $C_4H_{10} + 13\ F_2 \longrightarrow 10HF + 4\ CF_4$ -1510.2 kcal

Eq. 7: $C_2F_6 + 2/3\ NF_3 \longrightarrow 2CF_4 + 1/3\ N_2$ -104.1 kcal

Eq. 8: $CO_2 + 4/3\ NF_3 \longrightarrow CF_4 + O_2 + 2/3\ N_2$ -89.4 kcal

At the Naval Surface Weapons Center, limits of flammability were determined for mixtures of several other gaseous fuels and NF_3. The combustion chamber was a one-meter length of 10 cm I.D. clear plastic pipe, mounted vertically with a gas inlet at the top, a stirring shaft extending the length of the tube, and two 3mm diameter stainless steel electrodes at the bottom. The electrodes had a 3mm gap and were connected to a 9000 v., 13 ma power supply.

The range of flammability of n-butane/NF_3 mixtures was determined to be 1.5 to 75 mole percent butane and the effect of nitrogen diluent is shown in Figure 2. Most mixtures within the shaded area explode violently when sparked. The areas of flammability hazard for methane, ethane, and propane can be anticipated to lie between that of hydrogen and butane. Mixed with oxygen, butane is flammable only from 1.8 to 49 mole percent butane[6], and the area of flammability hazard shown in Figure 4 is about two-thirds that of the area in Figure 2. Not only is butane flammable over a wider range in NF_3 than in O_2, but as shown by Equations 4 and 5, it also releases more heat when burned in NF_3. For comparison, the heat released by the combustion of butane in F_2 is shown in Equation 6. Thermodynamic calculations indicate that maximum combustion temperatures are produced by fuel-rich mixtures, and Allan[7] has reported that the burning velocities of NF_3/hydrocarbon mixtures

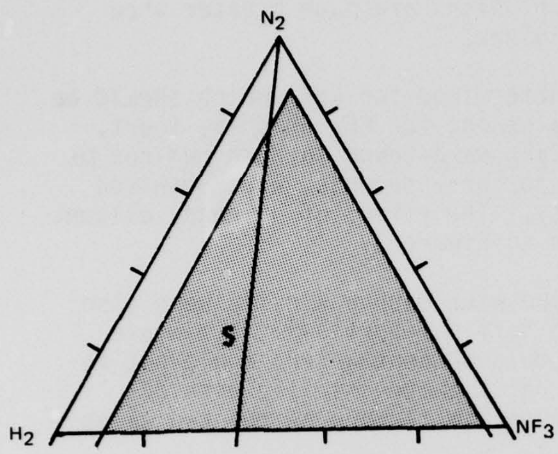

Figure 1. Limits of Flammability of $H_2/NF_3/N_2$ Mixtures (5)

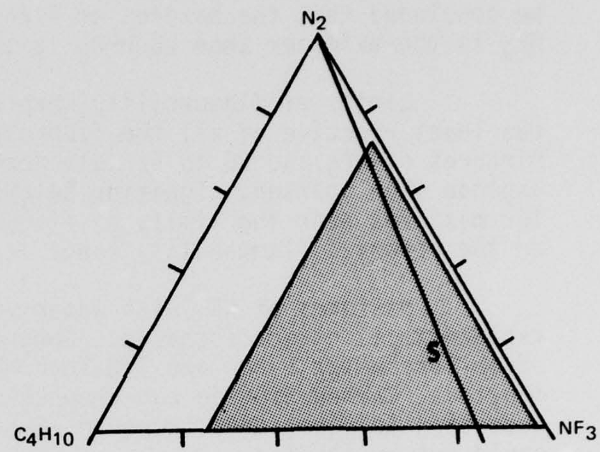

Figure 2. Limits of Flammability of $C_4H_{10}/NF_3/N_2$ Mixtures

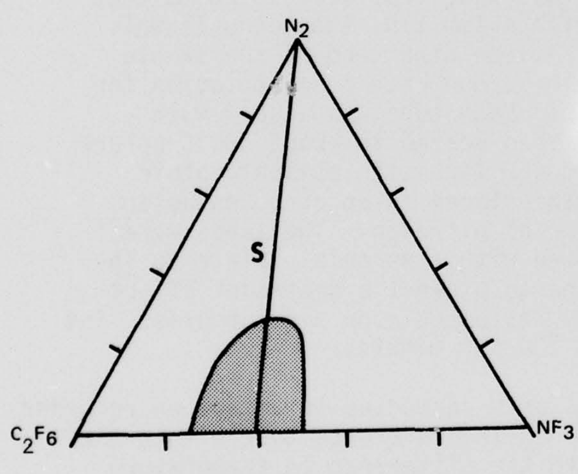

Figure 3. Limits of Flammability of $C_2F_6/NF_3/N_2$ Mixtures

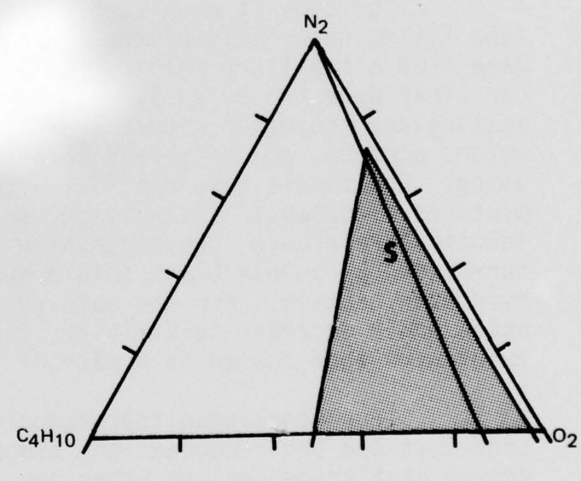

Figure 4. Limits of Flammability of $C_4H_{10}/O_2/N_2$ Mixtures

are about three times greater than that of O_2/hydrocarbon mixtures. It can be concluded that the hazards of fire or explosions are much greater when NF_3 is the oxidizer than when O_2 is the oxidizer.

Limits of flammability were also determined for C_2F_6 which should be the least reactive of all the fluorocarbons except for CF_4 which is inert. Mixtures of NF_3 and 26 to 52 mole percent C_2F_6 were found to burn but not to explode when sparked. Ignition delays, up to three seconds, were observed for mixtures near the limits of flammability. The effect of nitrogen diluent on the observed flammability range is shown in Figure 3.

Mixtures of NF_3 with water vapor and with carbon dioxide were also exposed to electric discharge. Contrary to Ruff's report(3,4), a mixture of 15 Torr water vapor and 740 Torr NF_3 (2 mole percent water) could not be ignited. Carbon dioxide can theoretically react exothermically with NF_3 according to Equation 8; however, a stoichiometric mixture of the two gases could not be ignited.

Reactions of NF_3 with gaseous fuels was also examined under considerably milder conditions. A differential thermal analysis apparatus (DTA) capable of examining gaseous samples was constructed. Work to be described later had indicated that NF_3 at elevated temperatures reacted with many materials. To minimize side reactions, the sample containers were fabricated entirely of glass.

The body of each sample container was made from a 16 x 150 mm test tube fitted co-axially at the closed end with a 1mm I.D. thermocouple well made from a capillary melting-point tube. At the other end of the sample container were two 10/30 $ ground glass joints, one with a constriction for sealing and the other with a break-seal tip. Each tube was washed with water, acetone, and methylene chloride and then heated to about 500°C before using. The sample tube was filled to about 400 Torr with stoichiometric mixtures of gases to be analyzed, sealed, and placed in an oven beside an identical reference tube containing 400 Torr of nitrogen. The tubes were surrounded by a thin brass shield and covered with a porcelain plate to insure even heating. For the same purpose and to prevent a heat-sink effect which would decrease sensitivity, the tubes rested only on pin supports. The tubes were then heated at a rate of 1.5 to 2°C per minute.

Iron-constantan thermocouple leads were connected to a two-pen recorder such that one pen recorded the temperature in the reference tube within one degree centigrade and the other pen recorded the difference in temperature between the sample and reference tubes. Reaction temperatures were taken as the initial departure of the exotherm or endotherm peaks from the base line.

The results are summarized in Table I, and the products listed were identified by gas chromatography. Nitrogen trifluoride reacted with the glass sample container at 273°C and the reactions with other gases at or above this temperature are questionable. Of the gas mixtures examined, only NF_3/trichloroethylene definitely reacted at a lower temperature, and this was also

the only endothermic reaction observed. A sample of trichloroethylene by itself exhibited only a slow exothermic decomposition beginning at 374°C. Nitrogen trifluoride/butane indicated a slow exotherm beginning at 231°C, but the heat produced was very small. Analysis of the reaction products did support the initiation of a reaction at this temperature. One reaction product was a relatively large amount of carbon, and Allan[7] has also reported the formulation of copious amounts of carbon in the combustion of butane with NF_3.

Benzene/NF_3 showed an exothermic reaction at the same temperature as did NF_3 alone, but the two components did not necessarily react directly with one another. The products contained a large amount of CO, and it is believed that the NF_3 first reacted with the glass, producing nitrogen oxides which in turn reacted with the benzene.

Carbon dioxide did not react with NF_3, and the exotherm and products are attributed only to the NF_3/glass reaction. Mixtures of water vapor, ammonia, or 2-propanol with NF_3 exothermed at temperatures higher than NF_3 alone, and these fuels may be sufficiently adsorbed on the glass so as to passivate it until higher temperatures. Water vapor and NF_3 produced a higher ratio of NO to NO_2 than did the NF_3/glass reaction; however, unreacted water was recovered and it was not conclusively determined if any had been consumed. As with benzene, 2-propanol and ammonia may have reacted either directly with NF_3 or with nitrogen oxides produced by an NF_3/glass reaction.

I. B. Reactions of NF_3 with Polymers

At room temperature NF_3 appears to be inert towards polymers. Even polyethylene film has been reported to show no observable deterioration after more than a month of exposure to NF_3[8]. However, compatibility data at elevated temperatures are lacking. At the Naval Surface Weapons Center, samples of polyethylene, polypropylene, polystyrene, poly-α-methylstyrene, Lucite, and silicone grease were examined both visually and by differential scanning calorimetry after six days of exposure to five atmospheres of NF_3 at 135°C. Comparisons were made with samples heated under N_2. All but Lucite and silicone grease showed a mild surface reaction.

In another study, samples of Kel-F valve packing,Teflon, Tetrafluor, Viton, Neoprene, silicone rubber, Buna-N, butyl rubber, and ethylene propylene were heated for six weeks at 150°C under 150 psi of NF_3. Similar samples were also heated under N_2. No changes were observed in the Teflon, Tetrafluor, Viton or Kel-F. Silicone rubber heated under N_2 was unchanged but the sample exposed to NF_3 was noticeably deteriorated. Although still flexible, it was covered with cracks, was less elastic, and appeared softer. Its shore hardness had dropped from 57 to 40. Neoprene had become considerably stiffer, harder, and brittle, and the other polymers showed extensive deterioration.

I. C. Reactions of NF_3 with Metals

Reactions of NF_3 with metals are characterized by the formation of N_2, N_2F_4, cis and trans N_2F_2, and metal fluorides. In their early work, Ruff et al[3] reported that Li, Na, and K react violently with NF_3 when heated above their melting points. Barium and zinc were reported to ignite when heated above 200°C, Pb and Cd formed fluoride coatings at their melting point, Hg formed a scum on heating, and B and Si ignited at about 500°C. Reported as less reactive were Cu, Ag, Fe, Ca, Al, Mg, As and Sb. Observed as unreactive were Mo, Bi, Cr, Ni, Co, W, Mn, Pt, P, C, and S.

At the Naval Surface Weapons Center, tests were conducted to determine: (1) the temperature required to ignite metals in an NF_3 atmosphere; (2) the temperature at which metals that are rapidly heated in NF_3 first exhibit a noticeable reaction; and (3) the effects on metals that are exposed for long periods to NF_3 at ambient or moderate temperatures. The heat released by the reaction of NF_3 with several metals is shown in Equations 9 through 14.

Eq. 9: $NF_3 + Al \longrightarrow AlF_3 + 1/2\ N_2$ -331.3 kcal

Eq. 10: $NF_3 + Ti \longrightarrow TiF_3 + 1/2\ N_2$ -313.4 kcal

Eq. 11: $NF_3 + Zr \longrightarrow ZrF_3 + 1/2\ N_2$ -305.3 kcal

Eq. 12: $2/3\ NF_3 + Mg \longrightarrow MgF_2 + 1/3\ N_2$ -248.9 kcal

Eq. 13: $NF_3 + Fe \longrightarrow FeF_3 + 1/2\ N_2$ -219.3 kcal

Eq. 14: $2/3\ NF_3 + Cu \longrightarrow CuF_2 + 1/3\ N_2$ -111.4 kcal

To determine the temperatures required to ignite metals in an NF_3 atmosphere, thin wire samples were directly heated by an electric current. With only the wire at an elevated temperature, reaction of NF_3 with other materials was avoided. As the current was increased, the change in resistance was calculated from continuous recording of voltage and current measurements. If changes in resistance due to corrosion can be neglected, the temperature of a wire can be calculated by the equation:

$$t = \frac{\Delta R}{\alpha P} + 20$$

where t is the temperature in °C, ΔR is the change in measured resistance from that at 20°C, P is the resistance of the wire at 20°C, and α is the temperature coefficient of the metal.

Wires of pure nickel, iron, copper, and aluminum were examined. Each had a diameter of 0.127 mm and was clamped between terminals 3 cm apart in a 110 ml closed bomb. The bomb was evacuated prior to filling with NF_3.

TABLE I

GAS PHASE DTA DATA FOR NF_3 REACTIONS

Reactant	Temperature, °C	Products
Glass	273 (Exo)	NO, NO_2, White Solid
CO_2	273 (Exo)	NO, NO_2, White Solid
H_2O	291 (Exo)	NO, NO_2, White Solid
C_6H_6	273 (Exo)	CO, N_2, CO_2, Unidentified Gas, Polymeric Film
NH_3	296 (Exo)	N_2, White Solid
$CH_3CH(OH)CH_3$	314 (Exo)	CO, CO_2, NO, Brown Solid
C_4H_{10}	231 & 285 (Exo)	N_2,NO,CO, Carbon,White Solid
$CHCl = CCl_2$	190, 208 (Endo) 249 (Exo)	NO, Colorless Liquid and Crystals
$CHCl = CCl_2$(Alone)	374 (Exo)	Dark Brown Oil

TABLE II

TEMPERATURES(°C) REQUIRED FOR METAL WIRES TO IGNITE IN OXIDIZING ATMOSPHERES

	Al	Cu	Fe	Ni
Melting Point	660	1083	1535	1455
Breaking Point under N_2	550	1080	1517	1385
Ignition Point under NF_3 (1 atm)	Inconsistant	550	817	1187
Ignition Point under NF_3 (100 psi)	Inconsistant	475	612	967
Ignition Point under F_2 (1 atm) (9)	Above M.P.	692	672	1153
Ignition Point under O_2 (1 atm) (10)	1750	1100	1300	Above M.P.
Ignition Point under O_2 (100 atm) (10)	1750	800	680	-

TABLE III

ADDITIONAL METAL IGNITION TEMPERATURES

	F_2 (9)	O_2 (10)	O_2 (100 ATM) (10)
Stainless Steel	681°C	1400°C	1300°C
Monel	396°C	-	-
Molybdenum	205°C	780°C	700°C
Brass	-	1100°C	800°C
Magnesium	-	640°C	640°C
Lead	-	850°C	850°C
Tungsten	283°C	-	-
Zinc	-	940°C	1200°C

TABLE IV

ESTIMATED MASS COMBUSTION RATES (G/Sec X 10^{-3})

	NF_3	O_2	Air
Iron	2.348	2.010	1.205
Aluminum	2.802	1.25	0.121
Nickel	8.565	-	0.194
Copper	6.911	6.410	3.476

Tests were done in atmospheres of 15 psi NF_3, 100 psi NF_3, and 15 psi N_2. Data for each metal are summarized in Table II. For comparison, Tables II and III also list data for the ignition of electrically heated wires under an atmosphere of F_2[9] and of O_2[10].

Under nitrogen atmosphere the wires broke near their melting points but none of them ignited. Under NF_3 all wires ignited, and nickel which is reported in the literature to be unreactive burned brilliantly.

Pictures at 100 frames per second were taken of Al, Cu, Fe, and Ni wires ignited in NF_3, O_2 and air. From these pictures, mass burning rates were calculated, as shown in Table IV.

The temperature at which metals that are rapidly heated in an atmosphere of NF_3 first exhibit a noticeable reaction was determined by differential scanning calorimetry (DSC). Powdered metal samples were heated at 20°C per minute in a DSC cell filled with an atmosphere of NF_3. Contrary to Ruff's observation[3], zinc powder did not react with NF_3 until about 300°C, and at that temperature it did not ignite. Successive heatings of the same sample rapidly eliminated the reaction at 300°C but a strong endotherm remained at the melting point of zinc, 418°C, suggesting that the surface of the metal had been passivated. Similarly, nickel powder appeared to become passivated at about 330°C, aluminum at 300-325°C, copper at 270-340°C, and silver at 350°C.

For comparison and in conflict with Ruff's observations, Glemser[11] has reported that Mo powder reacts with NF_3 at 280°C. Colburn and Kennedy[12] have reported the preparation of N_2F_4 in 62 - 71% yield from the reaction of NF_3 with Cu, Bi, As, Sb, or stainless steel in a flow reactor at 375°C and a residence time of about three minutes contradicting Ruff's observation that Bi is unreactive. Also contrary to Ruff's observation, Gould and Smith[13] found C to be readily reactive with NF_3 and have reported 75% conversion of NF_3 to N_2F_4 in a fluidized bed of carbon at about 440°C and a reaction time of only a few seconds. Dresden et al[14] have reported that NF_3 reacts with liquid Hg at 320 - 333°C in a flow system. About 60% of the NF_3 is converted to N_2F_4 and a small amount to cis N_2F_2. Others have reported that Hg vapor reacts readily with NF_3 in an electric discharge.

To determine the effects on metals after prolonged exposure to NF_3 at moderate temperatures, samples of the twelve metals listed below were exposed for 72 hours to 160 psi of NF_3 at 115°C and a second set of samples was exposed for 48 days to 225 psi of NF_3 at 25°C.

Aluminum 6061	Stainless Steel 347
Aluminum 5052	Monel 400
Aluminum 1100	Nickel 200
Aluminum 2024	Copper
Stainless Steel 321	Aluminum Brass
Stainless Steel 304	Admiralty Brass

After the exposure at 25°C, all of the samples except for aluminum alloys showed slight corrosion under examination with a scanning electron microscope. After the exposure at 115°C, all samples except the aluminum alloys exhibited visible tarnishing and weight increases. Under the scanning electron microscope, extensive crystal growth was observed on all except the aluminum alloys which showed only slight corrosion. Detailed studies of metalographic copper surfaces indicated that the corrosion by NF_3 occurred indiscriminately, suggesting a passivating reaction. There was no evidence of preferrential attack at crystal boundaries. Some of the alloys, particularly aluminum alloys, may react more along the grain boundaries but the data presently available are not conclusive.

II. Toxicity of NF_3

The first toxicity studies on nitrogen trifluoride were performed in 1931(15). Concentrations of 10,000ppm were fatal to mice after 40 minutes and to a cat after four hours. The deaths were caused by anoxia as a result of methemoglobin formation. In 1956, Jarry and Miller(16) reported that incompletely purified (90 percent) nitrogen trifluoride caused irritation of lung tissue comparable to that from nitrogen oxides but required much higher concentrations. However, the use of impure nitrogen trifluoride in these early experiments largely invalidates the results.

II. A. Chronic Toxicity of NF_3

The only available data on the chronic effects of NF_3 exposure were reported by Torkelson et al(17) at the Dow Chemical Company in 1962. They exposed rats to 100 ppm of nitrogen trifluoride for seven hours a day, five days a week over a period of 4-1/2 months. The rats at the end of this period appeared normal. There were no changes in behavior, heart, lungs, blood and no appearance of fluorosis. However, microscopic examination showed definite degenerative changes in the livers and kidneys of both male and female rats, with damage being more pronounced in the females.

The Dow group also reported good qualitative agreement in the results obtained by intraperitoneal injection and acute inhalation studies. Single exposures to greater than 1000 ppm caused deaths after four hours. Exposure to higher concentrations caused deaths in shorter periods of time. Enlarged spleens were found in many of the surviving rats. After intraperitoneal injection of 10 ml of undiluted nitrogen trifluoride, the rats appeared normal in behavior and activity. Autopsies revealed, however, gross enlargement of the spleen, damage to liver and spleen, myocardial degeneration and an increase in the fluoride content of blood, bones, and teeth. These results were taken to indicate there is a different mode of toxic behavior in acute as opposed to chronic exposures.

The Dow group concluded that their data were not sufficient to set a "No-effect"concentration level. They felt that additional experiments involving repeated exposures of several species for seven to eight hours at levels of 50 ppm or less were needed.

II. B. Acute Toxicity of NF_3

In 1968, a group at Oregon State University, Corvallis, Oregon investigated the pharmocology and metabolism of NF_3[18]. They found that a concentration of 10,000 ppm of NF_3 was lethal to rats after exposure times of 60 to 70 minutes. At this concentration, 60 to 70 percent of the available hemoglobin had been converted to methemoglobin. The formation of methemoglobin, however, is reversible and the level in rats exposed to sub-lethal concentrations rapidly returned to near-normal. They found that dogs exposed to 2500 ppm of NF_3 could reduce methemoglobin faster than it was formed and presumably could survive indefinitely or until chronic effects became paramount. They also state that at a concentration of 500 ppm the uptake of NF_3 in dogs ceased, but this conclusion is at variance with the data of Torkelson and should be viewed with suspicion. Other findings indicated a possible effect upon filtration or secretion mechanisms may be caused by acute exposure.

Other studies[19,20] by the Oregon State University group showed that NF_3 is almost innocuous to nonmammalian organisms.

A SysteMed Corp. Group[21,22,23] determined the LC_{50} values for NF_3 at 60, 30, and 15 minute exposure times. The LC_{50} values at 50 minutes for mice, rats, dogs and monkeys are respectively 7500, 6700, 9600 and 10,000 ppm. They also found that no detectable physiological changes occurred in dogs and monkeys at exposure levels of 1000 ppm for 30 minutes and 500 ppm for one hour. They proposed that the Emergency Exposure Limit (EEL) set by The National Academy of Sciences, National Research Council Committee on Toxicology (NAS-NRC) of 100 ppm for 30 minutes and 50 ppm for 60 minutes (3000 ppm minute) be raised to 30,000 ppm minutes. Recently, an EEL value of 22,500 ppm minutes based on Vernots(23) data has been recommended by the Naval Surface Weapons Center and established by NAS-NRC.

Foster[24] has studied the effects of NF_3 inhalation on the cardio-vascular system of rats. After exposure for one minute to 100 percent NF_3, there was a decrease in diastolic pressure, systolic pressure and heart rate. However, rats which inhaled oxygen for five minutes immediately after NF_3 exposure showed a temporary increase in diastolic pressure, systolic pressure and heart rate.

Coppoc and Leger[25] studied the effects of NF_3 of plasma concentrations of lactate and certain enzymes. They found a six-fold increase in blood lactate of rats exposed to 10,000 ppm of NF_3 for 45 minutes. This quickly returned to normal within four hours. Serum isocitric dehydrogenase did not change. Serum glutamic oxalacetic transaminase was unchanged at one hour but increased two to three times by six hours and remained elevated for as long as 24 hours. They, too, concluded that the toxicity of NF_3 cannot be explained solely on the basis of methemoglobin formation.

To sum up, exposure to large concentrations of nitrogen trifluoride can cause a rapid production of methemoglobin which returns to baseline levels five to ten hours after exposure. There is a slower increase of Heinz bodies which reaches a maximum a day or two after exposure. A gradual decrease in total hemoglobin occurs shortly after exposure and reaches a minimum in five days to two weeks. There is a similar decrease in red blood cells and hemotrocrit with a six percent increase in reticulocytes after three weeks. The symptoms are typical of Heinz body anemia. Dogs and monkeys almost always died within one hour after exposure to lethal concentrations. Many mice, however, survived for several hours, a few for one day, and one for three days. Those dying after one day showed extensive pneumonia[23].

Unfortunately a number of erroneous conclusions regarding the toxicity of NF_3 have entered the literature. These appear to be the results of "better safe than sorry" precautions taken at a time when the properties of NF_3 were poorly defined. It seems the tendency was to equate NF_3 with fluorine and/or HF or perhaps tetrafluorohydrazine. Fluorine and HF are corrosive gases while tetrafluorohydrazine is easily hydrolyzed giving rise to HF. On the contrary, NF_3 is only hydrolyzed with difficulty at elevated temperatures over relatively long periods of time. Thus, NF_3 should be innocuous insofar as skin contact is concerned. Buttressing this conclusion is the fact that there is no mention whatsoever of any skin damage occurring during any of the acute or chronic toxicity study carried out to date.

Nevertheless, it has been stated that skin contact must be avoided[26]. This is apparently based upon a Stauffer Chemical Company Technical Bulletin[27]. Recently, this same warning based upon these references has again been duly reported [29,30,31,32]. Thus, a Technical Data Sheet[29] by Air Products and Chemicals, Inc., Allentown, Pennsylvania states that first aid for NF_3 exposure is similar to treatment for HF. For skin contact they recommend: (a) a drenching shower of water, (b) removal of clothing while in the shower, (c) flushing of the exposed areas with a two to three percent aqueous ammonia solution followed by liberal rinses of water, (d) followed by an ice-cold saturated solution of magnesium sulfate or iced 70 percent alcohol, for 30 minutes, and (e) call a physician. Since skin and eye contact will necessarily occur upon inhalation, it is not quite clear how immediate oxygen administration in conjunction with eye irrigation can be carried out simultaneously with the above procedures for skin contact.

An October 1973 study by the J. J. Henry Company[30] recommends similar but somewhat more stringent first aid treatment. For skin contact they recommend a drenching cool shower for as long as two hours, the application of an iced solution of hyamine or other high molecular weight quaternary compounds (unspecified), and finally a generous quantity of thick paste made from magnesium oxide and glycerin. It should be noted that untrained personnel could unwittlingly use a quaternary ammonium hydroxide, a highly corrosive chemical, without violating the above instructions.

The Air Products Bulletin also states that the moldy, pungent odor of NF_3 is the best means of detection[29]. However, it has been determined that only one person of five tested could detect NF_3 by odor at a concentration of 500 ppm, a level at which physiological damage could occur. A statement in the same bulletin that "prolonged absorption of nitrogen trifluoride may cause mottling of the teeth and skeletal changes of osterosclerosis" is bemusing. The reference given in justification for this statment is the Merck Index[33], wherein it is stated "for chronic effects, see sodium fluoride". Again there is no experimental basis for equating NF_3 with sodium fluoride but while perhaps innocuous, it is illustrative of the types of unjustified comparisons that have been made and which still persist.

Warnings and treatment procedures for skin contact are coupled with similar warnings concerning eye contact. There are a number of observations in the literature that NF_3 can cause eye irritation[23,34], but irritation is said to be slight[35] without follow-up complications.

II. C. Safety Recommendations

The above references include the most reliable data on the toxicity of NF_3 available at this time[36]. Concurrence has been expressed by others with experience in the NF_3 field[35,37,38]. On this basis, in January 1975, the Naval Surface Weapons Center recommended revision of the EEL's for NF_3. The recommended revisions are applicable to military or space personnel and have since been established by the National Academy of Sciences - National Research Council, Committee on Toxicology as follows: 2250 ppm for ten minutes, 750 ppm for 30 minutes, and 375 ppm for 60 minutes.

A threshold limit value of 10 ppm, one-tenth of the concentration at which demonstrable histolic change has occurred[17] has been recommended by the American Conference of Governmental Industrial Hygienists[39]. This recommendation is however arbitrary, based on analogy with other oxidant gases, and should be retained only until more definitive data is available. It is recommended that chronic toxicity studies be carried out at a number of concentrations lower than 100 ppm to determine an accurate threshold limit value.

Instrumental monitoring of NF_3 levels is mandatory, preferably coupled with an automatic alarm system. Self-contained breathing apparatus should be present and readily accessible in working areas. The working areas should also be equipped with vacuum exhaust systems.

An individual exposed to massive concentrations of nitrogen trifluoride should be removed from the contaminated area as quickly as possible. Oxygen therapy should be begun at once by trained personnel preferably, if at all possible, under the direct supervision of a physician. Oxygen therapy should be continued for periods of up to six hours. The patient then should be allowed to rest under close supervision until all possibility of secondary complications

such as pneumonia can be discounted. Under no circumstances should the patient be placed in a situation where additional exposure to nitrogen trifluoride could occur until clinical symptoms of anemia have returned to normal. Treatment of secondary symptoms such as eye irritation should not be of primary consideration, but if bothersome to the patient, probably could be treated by the applications of a topical anesthetic during oxygen therapy.

III. Detectors for NF_3

The possible large-scale use of NF_3 has caused a need for an instrument to measure low concentrations of the gas in the atmosphere. Two types of applications arise: leak detection and long-term monitoring of storage and work areas. In most environments, NF_3 leak detectors need not be very discriminating against other gases. The main requirements are rapid response and good sensitivity to NF_3. On the other hand, long-term monitors should have good discrimination between NF_3 and other atmospheric contaminants. They can have a relatively slow response to low levels of NF_3 but do require good sensitivity and long-term stability.

III. A. Non-Discriminating Detectors

Leak detection of NF_3 can be readily accomplished with commercially available halogen leak detectors that have been designed for refrigeration repair work. Such instruments have sensitivities to NF_3 in the order of about one ppm or better. A small battery powered unit is available from TIF Instrument Company for about seventy-five dollars[40]. Several more sophisticated halogen detectors such as General Electric's "Feret" are more sensitive and can be calibrated for quantitative leak detections; however, they are considerably more expensive, less portable, and require more maintenance. These instruments detect many halogenated gases without discrimination, and they should not be used in explosive atmospheres.

III. B. Discriminating Detectors

Discriminating and quantitative techniques that have been studied for NF_3 detection are quadrupole mass spectrometry, electron capture gas chromatography, and laser or infrared spectral absorption. At the Naval Surface Weapons Center, an infrared detection method for NF_3 has been explored for both leak detection and long-term monitoring applications. Such a method measures at a spectral absorption frequency of NF_3, the intensity of infrared radiation passing through a sample of air. The decrease in intensity caused by the presence of NF_3 is a measure of its concentration. Figure 5 shows the absorption of NF_3 gas in the 900 cm^{-1} (27432 $ft.^{-1}$) region at a concentration of 17.5 ppm in a one meter (3.28ft.) path as measured by a Model 421 infrared spectrophotometer. Since an absorption of this same intensity would be obtained from one ppm of NF_3 in a 17.5 meter (57.4 ft.) path, it is evident that sensitivities well below one ppm can be achieved in a long path cell.

Since, in the infrared absorption method, any other gaseous contaminant which absorbs in the same spectral region as the gas being measured

will also give a signal, the identification of such interfering gases and the application of methods to eliminate or reduce their influence are an important aspect of the development of a useful infrared detector. A consideration of the intensities and frequencies of the NF_3 infrared absorption bands and of possible interfering gases, indicated that the 908 cm^{-1} (27676 $ft.^{-1}$) band of NF_3 was best suited for the detector application. An examination of possible interfering gases suggested that detection of NF_3 would be least subject to interferences if detected at 900 cm^{-1} rather than at the 908 cm^{-1} band center. Table V lists gases which were found to absorb significantly at 900 cm^{-1}. The absorption coefficient, k, is defined by the equation.

$$\ln (I/Io) = -k\, c\, l$$

where Io and I are the incident and transmitted intensities, respectively, c is the concentration and l is the path length. The sensitivity ratio is the sensitivity for the detection of NF_3, as compared to that of the interfering gas. This ratio also listed in Table V can be considered the parts per million of the interfering gas required to give the same absorption intensity as one ppm of NF_3.

The cis isomer of N_2F_2 also absorbs strongly at 900 cm^{-1} but its concentration can be expected to be low with respect to that of NF_3. In general, aliphatic and aromatic hydrocarbons do not absorb strongly at 900 cm^{-1}. Of the interfering compounds of Table V, the freons and cleaning solvents are expected to be most likely in the areas where NF_3 is to be stored or used. Ammonia may also be a likely contaminant. Fortunately, the NF_3 band exactly coincides with none of the 900 cm^{-1} region bands of these compounds. Therefore, further decreases in the sensitivity of the instrument to these contaminants can then be achieved by double-beam substraction techniques if it should prove necessary.

In order to determine the sensitivity of infrared detection of NF_3 at 900 cm^{-1}, an existing infrared monitor, designed for Otto Fuel II vapor detection was modified for use in the 900 cm^{-1} region. The optical layout of the modified instrument is shown in Figure 6. An f/4 beam from the heated ceramic rod S is transformed into an f/8 beam by mirror M_1 and directed into a long path cell. Multiple passes back and forth in the cell give path lengths from 3.25 to 20 meters (10.7 to 65.6 ft.). A path of 17.2 meters (56.4 ft.) was used in this work. Upon leaving the long path cell at a lower level, the beam is deflected by plane minors M_4 and M_5 and passes through a 13 Hz chopper to mirror M_7 which transforms the beam back to f/4. The beam is then further condensed by the optical lens, passes through the narrow-band filter F and is focused onto a pyroelectric radiation detector D. The detector output is amplified, demodulated and filtered by a lock-in amplifier and then displayed on a strip chart recorder. A considerable reduction in instrumental noise was achieved when the constant voltage ac supply which powered the infrared source was replaced by a highly stabilized dc supply.

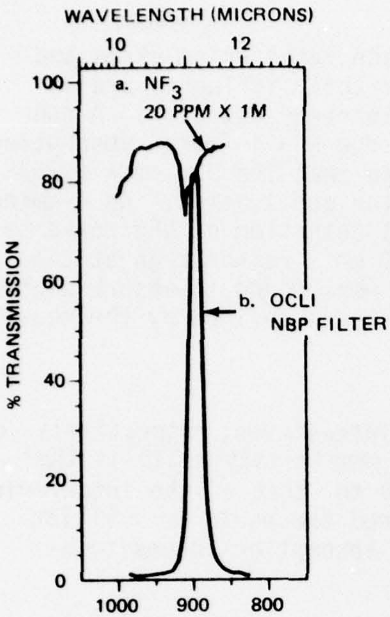

FIG. 5a ABSORPTION BAND OF NF_3 AT 17.5 PPM AND 1 METER PATH

5b TRANSMISSION OF BAND PASS FILTER

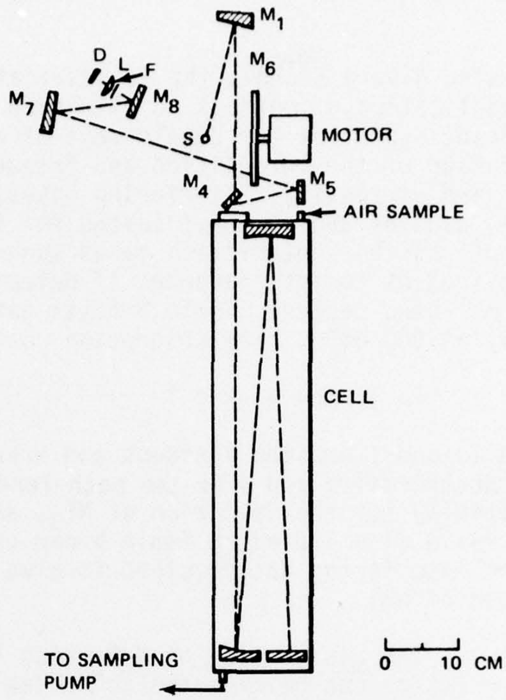

FIG. 6 GAS PHASE INFRARED DETECTOR FOR NF_3

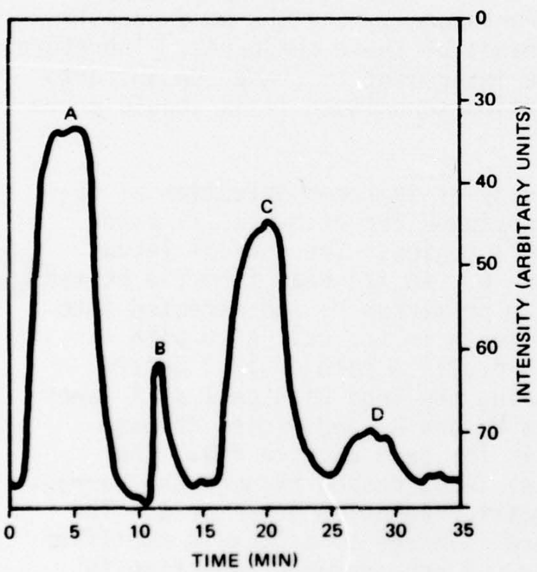

FIG. 7 DETECTOR RESPONSE TO VARIOUS NF_3 CONCENTRATIONS

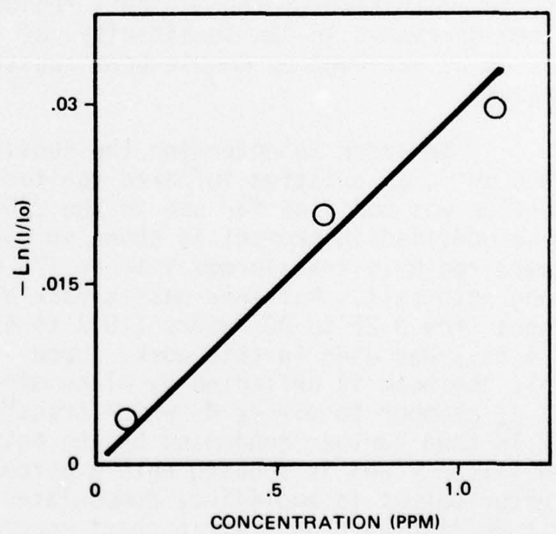

FIG. 8 INTENSITY VS CONCENTRATION – DATA OF FIG. 7

Table V

INTERFERING GASES

Gas	Absorption Coefficient at 900 cm^{-1}, $k(m^{-1}ppm^{-1}) \times 10^3$	Sensitivity Ratio, k_{NF_3}/k
NF_3	5.9	1
Nitric Acid	6.9	0.85
Freon 12	1.1	5.2
1,1-Dimethyl Hydrazine	0.90	6.5
2-Methoxyethanol	0.47	12
Hydrazine	0.46	13
1,3-Butadiene	0.39	15
Tetrachloroethylene	0.38	16
Freon 114	0.36	17
t-Butyl Alcohol	0.35	17
Tetrahydrofuran	0.26	23
1,4-Dioxane	0.23	26
Vinyl Chloride	0.21	28
Ethylene Oxide	0.18	32
Ammonia	0.12	50
Ethanol	0.075	79
Acetone	0.054	109

Discrimination against other atmospheric contaminants is realized in the instrument described here by a narrow band pass interference filter which transmits only radiation in a narrow band of frequencies, the center of which should be optimized both with respect to the band of NF_3 and to the bands of the possible interfering gases. The filter obtained for this study was an off-the-shelf item and not optimum for NF_3. Its spectral transmission curve is displayed in Figure 5. As was pointed out above in the discussion of interfering gases, a filter peaking in the range of 900-905 cm^{-1} would give both greater sensitivity to NF_3 and less to several of the interfering gases, particularly Freon 12.

A mixing system was set up to produce air samples with NF_3 concentration in the range of 0.01 to 10 ppm. The signals obtained with various mixtures in this range are shown in Figure 7. Peaks A, C, and D are responses to concentrations of 1.1 ppm, 0.6 ppm and 0.08 ppm, respectively flowing at 12-20 l/min. for periods of 2-4 minutes. The signal rises to a steady state and then returns to zero when the NF_3 injection into the sampled air is stopped. Peak B shows the response to a concentration of about 20 ppm for a few seconds. The rise time for this signal is characteristic of the electronic response of the instrument while the decay is chiefly determined by the flushing time of the long path cell volume (8 liters, 0.28 $ft.^3$). The peak heights of signals A, C, and D were used to calculate the absorbances at these three concentrations and the results are plotted in Figure 8. The deviations from a straight line are measures of the errors involved and include errors of mixing the various concentrations as well as errors in the measurement.

Measurement of the sensitivity of the instrument to Freon 12, showed that the sensitivity to Freon 12 is about 1/4 that to NF_3. The use of a band pass filter with a peak transmission at about 900 cm^{-1} would both increase sensitivity to NF_3 and decrease sensitivity to Freon 12 and give an estimated 5:1 sensitivity ratio (Table V). Further improvements can be realized by double-beam techniques.

From the results obtained, it is evident that an infrared detector for NF_3 operating at 900 cm^{-1} can reliably detect NF_3 to 50 ppb or less. In fact, a commercially available instrument, the Miran ambient gas analyzer, has been applied by commercial vendors to the detection of NF_3 in the one ppm range. This instrument is not sufficiently stable for long-term monitoring applications since it is a single-beam, direct-recording type. The Miran II infrared gas analyzer achieves long-term stability by using a ratio recording system. In the Miran II system, an intensity ratio is formed between radiation at the absorption frequency of the gas to be measured and radiation at a nearby frequency. The use of a separate reference frequency unfortunately doubles the problem of interference since absorption by another gas at either frequency will produce a false signal.

In order to achieve long-term stability, any system using spectral absorption techniques (uv, visible, laser, infrared, or microwave) must use ratio recording in order to eliminate variations in source intensity, window transmission, detector response and amplifier gain. A method that ratios between two paths, one containing the air to be sampled, the other NF_3-free air, at a single frequency (900 cm^{-1} for NF_3) offers some advantages over the Miran II frequency ratioing technique. In the two-path (double-beam) method, the problem of interfering gases is confined to a single frequency. With two paths available, the effects of interfering gases can be eliminated if the absorption frequencies of the interfering gases do not exactly coincide with those of the gas being measured. This is achieved by placing relatively high concentrations of the interfering gas in both beams, thus effectively removing radiation at those particular frequencies.

IV. Fire Extinguishment

When dealing with NF_3 propagated or initiated fires, it should be recalled that a high temperature NF_3 is a vigorously reactive oxidizer. Fire containment and extinguishment techniques suitable for F_2 fires can be used. One major difference must be stressed; NF_3 fires can be expected to generate more toxic gaseous products than F_2 fires. The source of NF_3 should be positively removed if at all possible, and personnel should be supplied with portable breathing units, <u>not</u> chemical cartridge respirators.

The energy released on combustion of fuels with NF_3 is much greater than with O_2,and Allan et al[41,42,43] have reported that NF_3/hydrocarbon mixtures burn about three times faster than the corresponding O_2/hydrocarbon mixtures. It should be recalled, however, that like O_2 at room temperature NF_3 can form mixtures with gaseous fuels. In the event of fire, excessive heat or sparks, areas which might contain NF_3/fuel mixtures would present a hazard of explosion and appropriate precautions are necessary. Fuels mixed with NF_3 would present a fire or

explosion hazard over a much broader range of concentrations than with O_2. In contrast, F_2 would generally not present this hazard as it would react with most fuels on contact too rapidly to form potentially explosive mixtures.

Perhaps the most effective extinguisher for fires involving massive quantities of NF_3 would be liquid nitrogen. It is completely inert, would present a large heat sink, and should not damage most equipment. The probable storage of NF_3 as a cryogenic liquid would necessitate its ready availability.

Carbon dioxide fire extinguishers have been recommended for areas where NF_3 is stored, moved or used. Gas phase DTA studies in this laboratory have indicated CO_2 to be inert towards NF_3 up to 400°C; however, CO_2 can theoretically react with NF_3 to generate considerable heat and produce toxic nitrogen oxides. As data indicating the minimum energy to initiate this reaction are not presently available, we cannot at this time recommend unconditionally the use of CO_2 as an extinguisher for fires involving massive quantities of NF_3. If the amount of NF_3 is small, CO_2 should be acceptable.

As a fire extinguisher, water can be delivered rapidly in large volumes but may damage otherwise salvagable equipment. The use of water may pose an additional hazard. At relatively low temperatures, near 300°C, water vapor reacts with NF_3 to produce HF, NO, and NO_2. The extent of this hazard may be substantially reduced in that all of these highly toxic gaseous products are water soluble and may be at least partially washed away with the bulk of the water. It would seem that water cannot be eliminated as a candidate fire extinguisher.

Dry ammonium phosphate or bicarbonate type fire extinguishers might generate hazardous quantities of HF and nitrogen oxides when subjected to NF_3 under fire conditions. They probably should not be used to extinguish NF_3 fires. However, aqueous solutions would be no more hazardous than plain water and might be better fire extinguishers.

Bromotrifluoromethane, Halon 1301, might generate highly toxic gaseous products and might react vigorously with burning metals. While it may in some situations be a useful fire extinguisher, it cannot be recommended at this time for use with NF_3 fires.

To inhibit propagation of NF_3 initiated fires, supply lines should be equipped with heat sinks or other flame and explosion arrestors. Analogous to F_2, once ignited, NF_3 supply lines might be expected to burn relatively slowly but explosions may occur and propagate through the lines. Valves can be automatically actuated by a burglar-alarm type device, i.e., wires wrapped around the supply lines.

To reduce fire and explosion hazards, cleaning procedures should be suitable for systems handling O_2 or F_2. Soft fluorocarbon valve seats and packings are generally not reliable for F_2 but should present less of a problem with NF_3. A line fire might, however, propagate back through a soft valve seat and back-up metal seated valves should be used.

V. Emergency Disposal of NF_3

Shipboard storage of NF_3 presents the potential of serious health, fire, and explosion hazards if the tanks rupture or leak. Development of emergency disposal methods for NF_3 are essential. This is not to be confused with the laser exhaust scrubber and ejector systems currently being developed, which deal mainly with disposal of HF, DF, and F_2 and which operate under a different set of constraints.

For a first approximation, the constraints for emergency disposal of NF_3 can be considered to be:

a. Quantity of NF_3 to be disposed: 420 kg (924 lbs.)
b. Time limitation for disposal: 5 to 10 minutes
c. Acceptable exhaust level for toxic gases: present EEL values for 30 minutes exposure
d. Acceptable disposal unit volume: less than 2 m^3 (70 ft^3)
e. Limitations of shipboard facilities, with respect to power, water, etc.: none

These are based in part on an NSRDC Shipboard study.

V. A. Disposal by Exhausting into Water or Venting into the Atmosphere

Disposal of NF_3 by exhausting it into water is impractical because it hydrolyzes extremely slowly and has very low solubility in water. Venting into the atmosphere is also impractical. Since NF_3 is approximately three times as dense as air, it can settle out and cause local areas to have NF_3 concentrations higher than the acceptable EEL value. To dilute the NF_3 below hazardous levels before venting would require a very large volume of air. For a five minute disposal time, the mass flow rate of NF_3 necessary for complete disposal is approximately 1400 g/sec. (3.09 lb/sec.). At 23°C (73.4°F), the density of NF_3 is 0.003 g/cc (0.187 lb/ft^3) and the density of air is 0.001 g/cc (0.069 lb/ft^3). The volumetric flow rate of air required to achieve an NF_3 concentration of 750 ppm (30 min. EEL) is 6 x 10^5 l/sec.(2.1 x 10^4 ft^3/sec.). This large air flow could be achieved but the mechanical blowers needed would be much larger than the acceptable disposal unit volume of 2 m^2 (70 ft^3).

V. B. Disposal by Reaction with Charcoal or Metals

The reaction of NF_3 with charcoal can be represented by the equation:

$$4/3\ NF_3 + C \longrightarrow 2/3\ N_2 + CF_4,\ \Delta H = 135.7\ \text{Kcal/mole}\ (538.5\ \text{BTU/mole})$$

Disposal of NF_3 via this reaction is highly exothermic but could be done in a fluidized bed where the heat transfer is excellent. Such a technique has been demonstrated for fluorine disposal[44]. A significant problem, however, is that the reaction of NF_3 and carbon can produce the highly toxic and hazardous intermediate N_2F_4. Gould and Smith[45] have reported a 75 percent conversion of NF_3 to N_2F_4 at 400°C (752°F) in a fluidized charcoal bed. Raising the temperature to 500-600°C (932-1112°F) should shift the reaction more towards N_2 formation, but the production of N_2F_4 could still be expected. Methods do exist to neutralize N_2F_4 but would result in a much more elaborate disposal system. Increasing the residence time in the bed should also decrease the intermediate N_2F_4, but a much larger bed and lower gas flow rate would be required. The system constraints could not be met.

For arguments very similar to those given above, disposal of NF_3 in a fluidized bed of metal particles also seems impractical.

V. C. Disposal by Reaction with a Solid Propellant

An ejector-scrubber for DF chemical lasers is currently being developed by Atlantic Research Corporation. The device consists of a solid propellant (ejector) impregnated with particles of Mg and MgO (scrubbers). Such a unit might conceivably serve also for NF_3 disposal. In principle, ignition of the solid grain would generate gases sufficiently hot to dissociate any NF_3 fed into the unit. The fluorine produced would react with Mg vapor, forming MgF_2. Addition of water to the product gases would shift the reaction equilibrium so that the remaining F_2 would then react with MgO. At present, sufficient data are not yet available to determine the feasibility of this approach to NF_3 disposal.

V. D. Disposal by Combustion with a Fuel

Emergency disposal of NF_3 by reaction with the laser fuel may be the simplest and most feasible method available if the present laser combustor can be modified to also serve as a disposal combustor. Both hydrocarbons and fluorocarbons are being considered as fuels. In principle, their combustion with NF_3 is essentially the same except for the formation of HF by hydrocarbons. Disposal of HF can be readily achieved with the laser scrubber or by exhausting the highly water soluble gas directly into the ocean.

In normal laser operation, excess oxidizer is used and the combustion products contain considerable elemental or atomic fluorine. If instead a fuel-rich mixture were used, the fluorine would be consumed. For example, a number of C_6F_6/NF_3 mixtures containing 15 weight percent He as a diluent have been reacted. This work has been conducted by TRW under Navy contract. A mixture containing 56 weight percent NF_3, 29 weight percent C_6F_6, 15 weight percent He (approximately 3 weight percent fuel-rich) gave a combustion temperature of 2082°K (3288°F) and produced 1900 ppm of unreacted fluorine, which is well above the 30 minute EEL value of 10 ppm. By cooling the combustion products to 1500°K (2241°F), the equilibrium is shifted and

the fluorine concentration is reduced to two ppm. The major gaseous species produced are all inert materials. A fuel-rich combustion also produces carbon which is not toxic but may contaminate much of the equipment.

Flow conditions necessary to dispose of all of the NF_3 in five minutes is about one-half of the reactant flow conditions under normal laser operation, and the effluent gas stream would be flowing at approximately 2.4 kg/sec. (5.3 lb/sec.).

Modification of the present DF chemical laser combustor to serve also as a disposal combustor would require programming the combustor to change the fuel/oxidizer ratio on command. The remaining portion of the laser would then be used to cool the combustion products. If modification of the combustor is not feasible, a separate unit can be used. Even a water-cooled pipe might serve as an acceptable reaction chamber. Such a separate device can be programmed to burn any readily available fuel, even diesel oil.

SUMMARY

Many literature sources contain erroneous information on the toxicity of NF_3 and on the proper treatment for exposure to it. A new EEL value of 22,500 ppm-minute has recently been established and the present TLV should be examined for validity.

Commercially available halogen leak detectors can detect NF_3 at concentrations of one ppm or less but cannot distinguish it from other halogenated gases. An improved IR detector for NF_3 operating at 900 cm^{-1} has been assembled. The device can detect NF_3 to 50 ppb or less with little or no interference from other atmospheric contaminants.

The reactivity and the fire or explosion hazards of NF_3 at room temperature appear to be similar to that of oxygen but become more like that of fluorine as the temperature is increased. Nitrogen trifluoride can form readily ignitable explosive mixtures with many gaseous fuels and appropriate caution must be exercised in handling,storage and fire-fighting procedures.

Of the techniques that have been evaluated for the emergency disposal of NF_3, the most promising one appears to be combustion with excess of either a hydrocarbon or fluorocarbon fuel, and the present laser combustor might serve also as the disposal unit.

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